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# Metallic Copper Clusters Decorating Cu Ferrites Revealed by Deep Data Analysis

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With improved performance of TEMs and spectrometers, the limiting step for better materials characterization is now the ability to translate large datasets into meaningful information. Here, we present a new, semi-supervised method for retrieving spectral components and their respective spatial contribution that is efficient when weak spectral features are scattered in the spectrum-image (SI).

The sample is made of nanoparticles (NPs) produced by injecting an equimolar ratio of Cu and Fe nitrates solution in an induction Ar/$O_2$ plasma reactor. XRD analyses indicated the presence of $CuFe_2O_4$ tetragonal phase (33% wt), $Cu_{0.5}Fe_{2.5}O_4$ (47% wt) and (Cu,Fe)O (20% wt). The NPs were dispersed in ethanol on a lacey carbon TEM grid. The analyses were performed with an objective lens aberration corrected FEI Titan TEM operated at 300 kV and equipped with an annular detector and a Gatan Quantum image filter.

Fig. 1a shows nanoparticles decorated with a secondary phase. X-ray diffraction (not shown) combined with the HREM confirms that the NPs adopt the cubic and tetragonal phase of Cu ferrites (Fig. 1b). However, the low crystallinity of the secondary phase (Fig. 1c) makes it difficult to identify it using HREM. Wet tried using the Cu $L_{2,3}$-Fe $L_{2,3}$ signal to generate a bivariate histogram to isolate the Cu-rich regions of the SI, but a good compromise between the signal-to-noise ratio (SNR) and the "purity" of the metallic Cu character could not be achieved. Given the scarcity of pure Cu pixels, various versions of Independent Component Analysis [1] failed to produce physically sound components although the Bayesian Linear Unmixing with a NFINDR initialization [2] showed potential.

We used a Multivariate Curve Resolution (MCR) algorithm to extract physically meaningful spectra ($S$) and composition maps ($C$) from an image ($X$). The loglikelihood variant (MCR-LLM) has been shown to perform particularly well in low SNR datasets [3]. In this work, a hierarchical version of MCR-LLM was used to deal with local composition gradients and faulty pixels. Fig. 1d illustrates the methodology in which spectral features are extracted dyadically with each step. The 137×93 spectra were thus reduced to 331 significant ones from which we selected 4 (Fig. 1e): Cu (red), Cu ferrites (green), carbon (blue: featureless exponential background) and the hole (yellow: noise). The maps (Fig. 1f) associated with each spectrum were generated by finding the set coefficients that maximizes the loglikelihood [3]. This method is especially suited for datasets with low signal-to-noise levels contaminated with Poisson noise.

The EELS Fe:Cu:O intensity ratio of the Cu ferrite phase is consistent with $Cu_xFe_{3-x}O_4$ ($0 \leq x \leq 1$). The Cu content of the metallic Cu approached 70%, but was found along Fe (10% at) and O (20% at). The Cu $L_{2,3}$ edge profile is mostly metallic and the shape of the O K edge is indicative of the presence of (Cu,Fe)O, demonstrating that metallic Cu is mixed with the monoxyde. Comparing the spatial distribution of Cu clusters (Fig. 1f) with the Sobel-filtered STEM image taken from the same ROI (Fig. 1g), it can be inferred that the protrusions on the Cu ferrites NPs correspond to Cu-rich zones. The presence of Cu buds on the Cu ferrites are sought to form during solidification of the liquid droplets as the excess Cu is expelled. Cu then oxidizes in presence of the residual oxygen in the reactor or the air.

Unlike traditional methods, the exponential background is conserved and there is no need to sacrifice spatial resolution to increase the signal-to-noise ratio. In this case, a precise evaluation of the composition is achieved by the analysis of the endmember spectra rather than the background-subtracted signal of individual pixel. This work highlights the multiple opportunities of deep data analysis provided by advanced latent variable decomposition methods for the optimal interpretation of SIs [4].

References:

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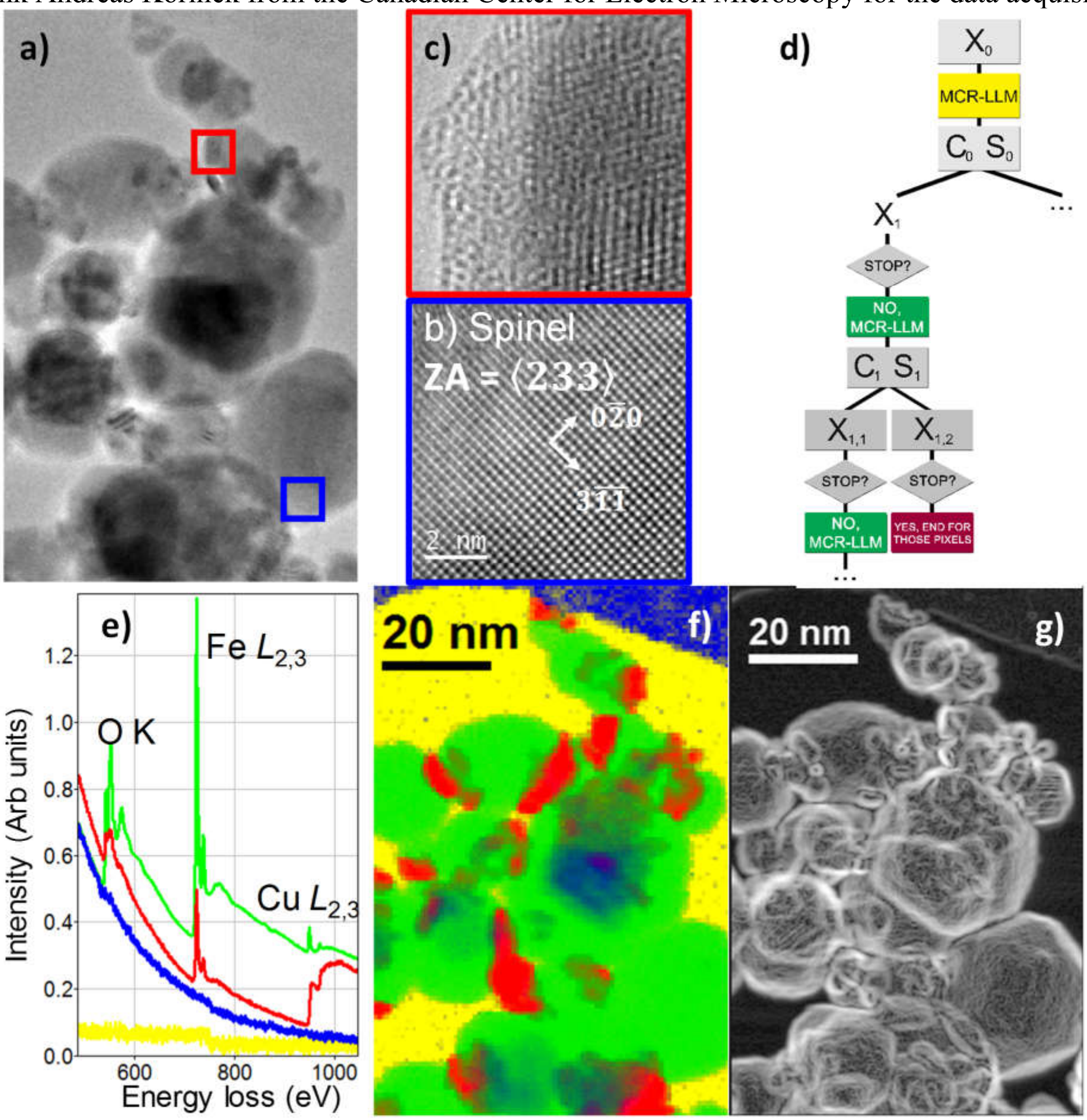


*Figure 1. (a) HREM micrograph. HREM image of a Cu ferrite nanoparticle (b) and a Cu-rich zone (c). (d) Algorithm used for the hierarchical method for classifying the spectra. (e)EELS spectra of the 4 characteristic regions (Green: Cu ferrite, Red: Cu, CuO, Blue: carbon lacey film and Yellow: hole). (g) Sobel-filtered STEM HAADF image of the same ROI as (a) and (f).*